

# Classifying Possible Tilting of Oxygen Octahedra in Perovskites

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The list of possible commensurate phases obtained from the parent tetragonal phase of perovskites by allowing the tilting of octahedra of oxygen ions is reexamined. It is found that many structures allowed by symmetry are not consistent with the constraint of very rigid octahedra.

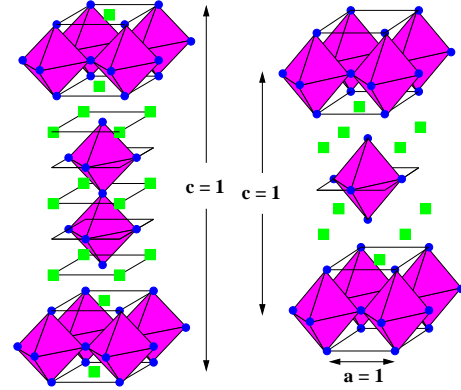
Many perovskite systems such as the Ruddlesden-Popper compounds [1]  $\text{K}_2\text{MgF}_4$ ,  $\text{Ca}_3\text{Mn}_2\text{O}_7$  are constructed from layers of corner sharing octahedra of F's or O's. These systems exhibit many interesting technological properties such as high  $T_c$  superconductivity[2], colossal magnetoresistance,[3] metal insulator transitions,[4] and coupled ferroelectric and magnetic order.[5,6] Many of these properties depend sensitively on the structural distortions from the ideal tetragonal  $I4/mmm$  structure (see Fig. 1) of space group #139 [space group numbering is from Ref. 7] which appear at structural phase transitions.[8–12] Accordingly, the accurate characterization of their structure is essential to reach a detailed understanding of their properties and then to fabricate new systems with enhanced desired properties. It is not surprising then, that one of the well known theoretical problems in crystallography is to list the possible structures that can be obtained by cooperatively reorienting the oxygen octahedra under the constraint of the shared vertices. The two principal approaches to this problem have been a) a direct enumeration of likely structures[13] and b) the use symmetry.[14] This last approach utilizes the celebrated computer program[15] to generate isotropy subgroups tabulated in Ref. 16. Using this tabulation Hatch *et al.* [14] gave a listing for the  $\text{K}_2\text{MgF}_4$  (214) structure of possible irreducible representations (irreps) for distortions by octahedral rotations. This listing was shown to be consistent with the revised results of method a).[14] This important work has stood unchallenged for over a decade.[17] However, here we will show that some of the listed structures are a) counterintuitive and b) inconsistent with the fourth order term in the Landau expansion for rigid octahedra, whose form is less general than allowed by symmetry.

To see this phenomenon in its simplest guise, consider a system with two order parameters  $Q_1$  and  $Q_2$  related by symmetry, for which the free energy assumes the form

$$F = (T - T_0)[Q_1^2 + Q_2^2] + u[Q_1^2 + Q_2^2]^2 + vQ_1^2Q_2^2 \quad (1)$$

up to fourth order in  $Q$  with  $u > 0$ . As the temperature is lowered through the value  $T_0$  the nature of the ordering depends on the sign of  $v$ . If  $v$  is positive, then ordering has either  $Q_1$  or  $Q_2$  zero. If  $v$  is negative, the ordering occurs with  $|Q_1| = |Q_2|$ . Only at the multicritical point[19] where  $v$  is zero (and also a similar sixth order anisotropy vanishes) can one have ordering in an arbitrary direction of order parameter space. One may also reach such a state via a first order transition, but for octahedral rota-

FIG. 1: (Color online) Structure of  $\text{A}_3\text{B}_2\text{O}_7$  (left) and  $\text{A}_2\text{BF}_4$  (right). The green squares are A ions. The B ions are at the centers of the oxygen (blue dots) octahedra.

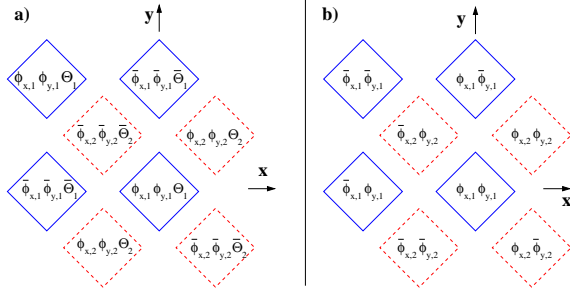


tions this is a very unlikely scenario, as we will explain. However we will find that in some cases the sign of  $v$  is fixed by the intraoctahedral constraint. In view of this discussion it seems preferable to predict possible phases from the form of the free energy for rigid octahedra.

As in the symmetry-based analyses, our discussion for the 214 structure will treat only commensurate structural phase transitions involving high symmetry wave vectors at the star of  $\mathbf{X} = (1/2, 1/2, 0)$ , of  $\mathbf{N} = (1/2, 0, 1/2)$ , or of  $\mathbf{P} = (1/2, 1/2, 1/2)$ . [18] Since  $\mathbf{X}$  is the simplest case, we will discuss it explicitly here.

Instead of dealing with irreps, we will consider the most general structure (shown in Fig. 2) which can be constructed using the angular distortions at the  $\mathbf{X}$  wave vectors providing that the octahedra rotate as constrained by their shared vertex. As noted in Ref. 14, when one plane of octahedra are cooperatively rotated through an angle  $\phi$  by moving the shared vertices, the displacement of this vertex relative to what it would be if it were not also part of an adjoining octahedron is of order  $\phi^2$ . Thus the intraoctahedral elastic energy will be quartic in the angular variables of each plane and we introduce an expansion parameter  $\lambda \gg 1$  which is the ratio of the intraoctahedral force constants to the other force constants of the lattice. Since interactions between octahedra in *different layers* do not involve these large intraoctahedral force constants, there are no interlayer couplings of order  $\lambda$ . Therefore we write the elastic free energy for the structure of Fig. 2 for the star of  $\mathbf{X}$  as

FIG. 2: (Color online) The structure of corner-sharing octahedra. The solid (dashed) squares are the cross sections of octahedra in the plane at  $z = 0$  ( $z = 1/2$ ). For clarity the octahedra are slightly separated instead of sharing vertices. Here  $\phi_x$  means that the  $+x$  vertex moves up by an amount  $\phi_x$  and the  $-x$  vertex moves down by an amount  $\phi_x$  and similarly for  $\phi_y$  and  $\theta$  is the angle of rotation about the  $z$  axis. Also  $\bar{Q}$  denotes  $-Q$ . Left: For the star of **X** and **P**. Right: For the star of **N**. For **X** the structure is invariant under  $z \rightarrow z + 1$ . For **N** and **P** the variables change sign under  $z \rightarrow z + 1$ .



$$F = A\lambda[\theta_1^4 + \theta_2^4] + B\lambda[\phi_{x,1}^4 + \phi_{x,2}^4 + \phi_{y,1}^4 + \phi_{y,2}^4] + C\lambda[\theta_1^2(\phi_{x,1}^2 + \phi_{y,1}^2) + \theta_2^2(\phi_{x,2}^2 + \phi_{y,2}^2)] + D\lambda[\phi_{x,1}^2\phi_{y,1}^2 + \phi_{x,2}^2\phi_{y,2}^2] + F_2, \quad (2)$$

where  $F_2$  is the free energy quadratic in the angles  $\theta$  and  $\phi$ . Here and below, because of the octahedral constraint quartic terms of the form  $\theta_1^2\theta_2^2$ ,  $\phi_{x,1}^2\phi_{y,2}^2 + \phi_{x,2}^2\phi_{y,1}^2$ , and  $\phi_{x,1}\phi_{y,1}\phi_{x,2}\phi_{y,2}$  which are allowed by symmetry (see Table I) do not appear at order  $\lambda$ . As explained below, other variables such as the displacements of nonoctahedral ions do not affect the symmetry of the phase we obtain. Using Table I, we see that the quadratic terms which are invariant under the symmetry operations are

$$F_2 = \alpha[\phi_{x,1}^2 + \phi_{y,1}^2 + \phi_{x,2}^2 + \phi_{y,2}^2] + 2\beta[\phi_{x,1}\phi_{y,2} + \phi_{x,2}\phi_{y,1}] + \gamma[\theta_1^2 + \theta_2^2]. \quad (3)$$

Since the angles are of order  $\lambda^{-1/2}$ , to evaluate  $F$  to order  $1/\lambda$ , we do not need to keep interoctahedral interactions of higher than quadratic order.

The structural phase transitions which we are investigating arise when *one* of the channels becomes unstable, i. e. when  $\gamma$  or  $\alpha - |\beta|$  passes through zero. For instance, when only  $\gamma$  becomes negative, then

$$\phi_{x,1} = \phi_{x,2} = \phi_{y,1} = \phi_{y,2} = 0, \quad (4)$$

so that

$$F = A\lambda[\theta_1^4 + \theta_2^4] - |\gamma|[\theta_1^2 + \theta_2^2], \quad (5)$$

which, when minimized, leads to

$$|\theta_1| = |\theta_2| = [-\gamma/(2A\lambda)]^{1/2}, \quad (6)$$

TABLE I: Effect of symmetry operations on the variables of Fig. 2.  $\mathcal{R}_4$  is a four-fold rotation,  $m_d$  and  $m_z$  are mirrors that take  $x$  into  $y$  and  $z$  into  $-z$ , respectively and  $T$  is the translation  $(1/2, 1/2, 1/2)$ . These variables are odd under the translations  $T_x = (1, 0, 0)$  and  $T_y = (0, 1, 0)$ .

|              | $\mathcal{R}_4$ | $m_d$        | $m_z$         | $T$          |
|--------------|-----------------|--------------|---------------|--------------|
| $\phi_{x,1}$ | $\phi_{y,1}$    | $\phi_{y,1}$ | $-\phi_{x,1}$ | $\phi_{x,2}$ |
| $\phi_{y,1}$ | $-\phi_{x,1}$   | $\phi_{x,1}$ | $-\phi_{y,1}$ | $\phi_{y,2}$ |
| $\theta_1$   | $\theta_1$      | $-\theta_1$  | $\theta_1$    | $\theta_2$   |
| $\phi_{x,2}$ | $-\phi_{y,2}$   | $\phi_{y,2}$ | $-\phi_{x,2}$ | $\phi_{x,1}$ |
| $\phi_{y,2}$ | $\phi_{x,2}$    | $\phi_{x,2}$ | $-\phi_{y,2}$ | $\phi_{y,1}$ |
| $\theta_2$   | $-\theta_2$     | $-\theta_2$  | $\theta_2$    | $\theta_1$   |

which gives Cmca (64), one of the three  $\theta$ -dependent structures for the star of **X** in Refs. 14 and 17. We do not allow the other two structures of Refs. 14 and 17 which have  $|\theta_1| \neq |\theta_2|$  because the octahedral constraint leads to  $v = -2u$  in the language of Eq. (1). Furthermore, the two solutions we omit are counterintuitive. Imagine building up the structure layer by layer. Let the first layer have  $\theta = \theta_1$ . The value of  $\theta$  for the second layer is not fixed because of the frustration resulting from the four-fold symmetry. The sign of  $\theta$  for the third layer is *not* frustrated and is  $\pm\theta_1$ , the sign depending on the details of the interatomic interactions. Thus  $|\theta_n| = c$  and we have two choices: either  $\theta_{n+2} = \theta_n$  (ferro) or  $\theta_{n+2} = -\theta_n$  (antiferro). The ferro (antiferro) configuration comes from the star of **X** (**P**). The relative phase of the even and odd numbered layers is a degeneracy similar to that in the body centered tetragonal antiferromagnet.[21,22]

Now drop the  $\theta$  variables, so that[23]

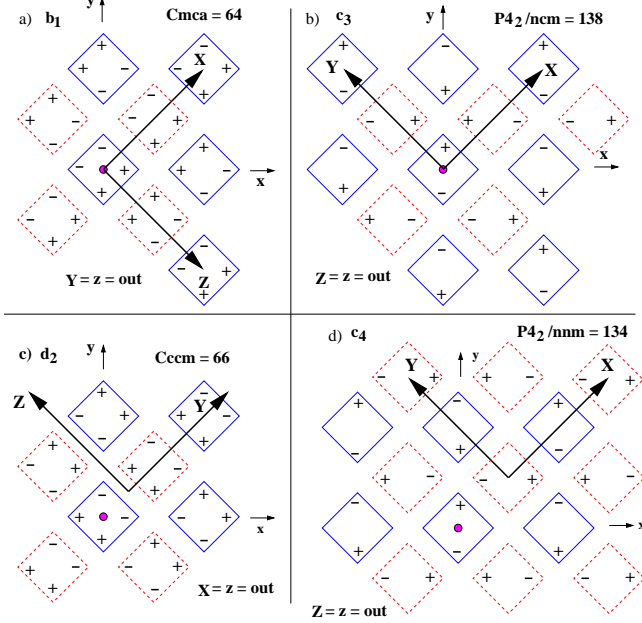
$$F = B\lambda[(\phi_{x,1}^2 + \phi_{y,1}^2)^2 + (\phi_{x,2}^2 + \phi_{y,2}^2)^2] + (D - 2B)\lambda[\phi_{x,1}^2\phi_{y,1}^2 + \phi_{x,2}^2\phi_{y,2}^2] + [(\alpha - \beta)/2][(\phi_{x,1} - \phi_{y,2})^2 + (\phi_{x,2} - \phi_{y,1})^2] + [(\alpha + \beta)/2][(\phi_{x,1} + \phi_{y,2})^2 + (\phi_{x,2} + \phi_{y,1})^2]. \quad (7)$$

There are four directions of the ordering vector  $\Psi \equiv [\phi_{x,1}, \phi_{y,1}, \phi_{x,2}, \phi_{y,2}]$  depending on whether or not  $\alpha - \beta$  becomes critical (negative) before  $\alpha + \beta$  and whether or not  $D > 2B$ .

When  $\alpha - \beta$  is critical and  $D < 2B$  then  $\Psi$  is proportional to one of  $a_1 = [11\bar{1}\bar{1}]$ ,  $b_1 = [1\bar{1}1\bar{1}]$ ,  $c_1 = [\bar{1}1\bar{1}1]$ , or  $d_1 = [\bar{1}\bar{1}11]$ . If  $\alpha + \beta$  is critical and  $D < 2B$ , then  $\Psi$  is proportional to  $a_2 = [1111]$ ,  $b_2 = [1\bar{1}\bar{1}\bar{1}]$ ,  $c_2 = [\bar{1}11\bar{1}]$ , or  $d_2 = [\bar{1}\bar{1}11]$ . If  $\alpha - \beta$  is critical and  $D > 2B$ , then  $\Psi$  is proportional to  $a_3 = [100\bar{1}]$ ,  $b_3 = [0\bar{1}10]$ ,  $c_3 = [01\bar{1}0]$ , or  $d_3 = [\bar{1}001]$ . If  $\alpha + \beta$  is critical and  $D > 2B$ , then  $\Psi$  is proportional to  $a_4 = [1001]$ ,  $b_4 = [0\bar{1}\bar{1}0]$ ,  $c_4 = [0110]$ , or  $d_4 = [\bar{1}00\bar{1}]$ . The four choices are equivalent:  $\mathcal{R}_4 b_n = a_n$ ,  $c_n = T_x b_n$ , and  $d_n = T_x a_n$ . Fig. 3 shows these solutions.

Now we identify the space groups of the structures of Fig. 3. The generators of  $b_1$  are  $(X \pm 1/2, Y + 1/2, Z)$ ,  $(X, Y, Z + 1)$ ,  $(\bar{X}, \bar{Y}, \bar{Z})$ ,  $(\bar{X}, Y, Z)$ , and  $(\bar{X} + 1/2, \bar{Y}, 1/2 + Z)$ , of  $c_4$  are  $(X + 1, Y, Z)$ ,  $(X, Y + 1, Z)$ ,

FIG. 3: (Color online) As Fig. 2 for the star of  $\mathbf{X}$  (with invariance under  $z \rightarrow z + 1$ ).  $x, y$  are the tetragonal axes and  $X, Y$ , and  $Z$  are the conventional lattice vectors after distortion. The filled magenta circle is the tetragonal origin.  $\Psi = [1\bar{1}\bar{1}]$  for a),  $[01\bar{1}0]$  for b),  $[\bar{1}\bar{1}\bar{1}]$  for c), and  $[0110]$  for d). The new origin is in the  $z = 0$  plane, except for c) where  $z = 1/4$ . Also  $\mathbf{X} \cdot (\mathbf{Y} \times \mathbf{Z}) = 2$ .

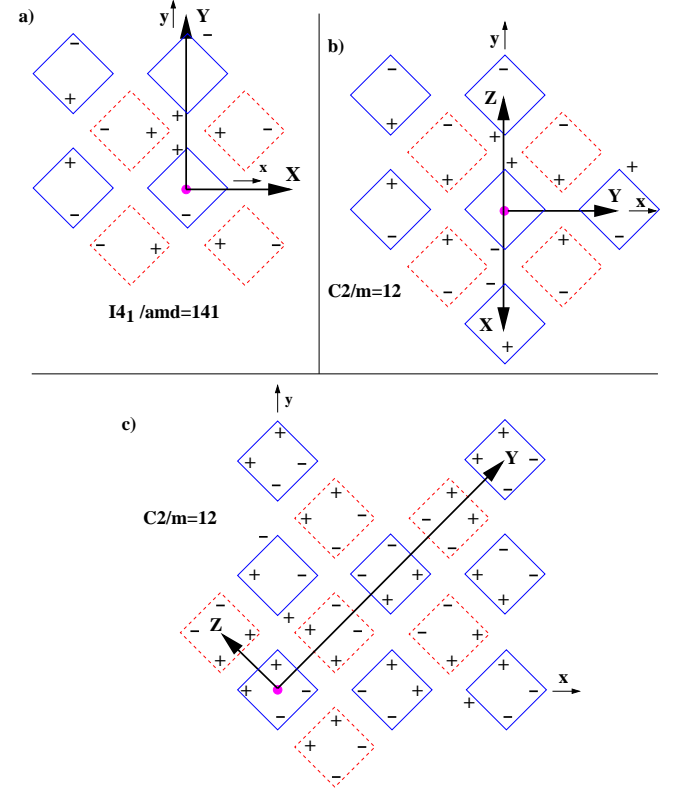


$(X, Y, Z + 1)$ ,  $(\bar{X}, \bar{Y}, \bar{Z})$ ,  $(\bar{Y} + 1/2, X, Z + 1/2)$ , and  $(X, \bar{Y} + 1/2, \bar{Z} + 1/2)$ , of  $d_2$  are  $(X \pm 1/2, Y + 1/2, Z)$ ,  $(X, Y, Z + 1)$ ,  $(\bar{X}, \bar{Y}, \bar{Z})$ ,  $(X, Y, \bar{Z})$ , and  $(X, \bar{Y}, 1/2 + Z)$ , and of  $c_3$  are  $(X + 1, Y, Z)$ ,  $(X, Y + 1, Z)$ ,  $(X, Y, Z + 1)$ ,  $(\bar{X}, \bar{Y}, \bar{Z})$ ,  $(\bar{Y} + 1/2, X, Z + 1/2)$ , and  $(X + 1/2, \bar{Y}, \bar{Z} + 1/2)$ . In comparison to Ref. 14 we omit the structures of space groups Pccn and Pmmm. These structures require accessing the multicritical point where  $D = 2B$ .

Similarly, we obtain the structure for the star of  $\mathbf{N}$  as in Fig. 1. The ordering vector  $\Psi$  is one of three types shown in Fig. 4:  $[1, 1, 1]$  which is  $C2/m$  (12),  $[0101]$  which is a different  $C2/m$  structure, or  $[0110]$  which is  $I4_1/amd$  (141). For the star of  $\mathbf{N}$  we do not find the eight structures listed in Ref. 14 which lead to first order transitions because these can only appear when the Landau expansion is carried to higher order (which we discuss later). In addition, Ref. 14 lists two space groups Cmmm (65) for which  $\Psi = [1000]$  and  $I4_1/mmm$  (139) for which  $\Psi = [1100]$ . Both these are inconsistent with the fourth order terms arising from the rigid octahedral constraint. They are also counterintuitive in that they both describe states in which ordered and disordered planes of octahedra alternate [see the discussion below Eq. (6)].

For the star of  $\mathbf{P}$  the possible structures are those of the left panel of Fig. 1 (with the variables changing sign under  $z \rightarrow z + 1$ ). The only  $\theta$ -dependent structure has  $\theta_{n+2} = -\theta_n$ ,  $I4_1/acd$  (142), and is one of the three structures listed in in Refs. 16 and 17. The other two struc-

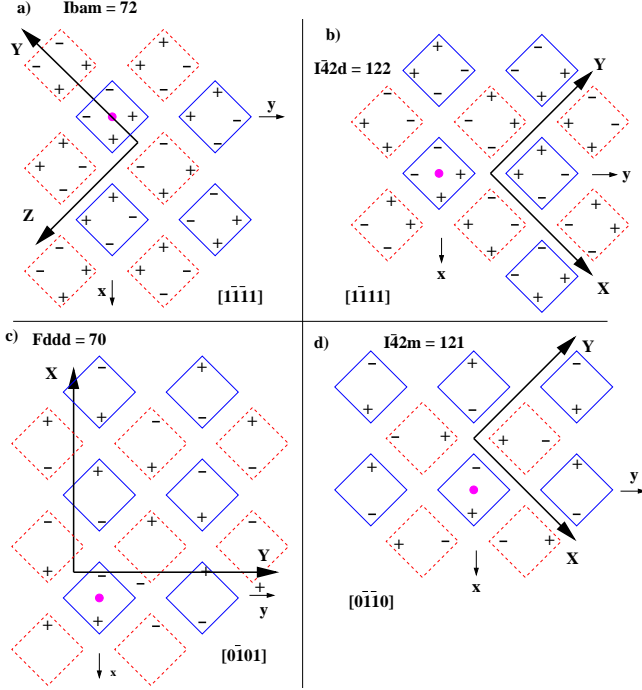
FIG. 4: (Color online) As Fig. 3 for the star of  $\mathbf{N}$  (with sign change under  $z \rightarrow z + 1$ ) for a)  $[01\bar{1}0]$ , b)  $[010\bar{1}]$ , and c)  $[\bar{1}\bar{1}\bar{1}]$ .  $x, y$  are the tetragonal axes, and  $X, Y$ , and  $Z$  are  $[(200)]$ ,  $(020)$ ,  $(002)$  in a),  $[(0\bar{1}1)$ ,  $(100)$ ,  $(011)]$ , in b), and  $[(002), (220), (-1/2, -1/2, -1/2)]$  in c).



tures listed there are not admissible as explained below Eq. (6). Now consider the  $\phi$ -dependent solutions. The four allowable types of ordering vectors are  $[1010]$ ,  $[1001]$ ,  $[1111]$ , and  $[11\bar{1}\bar{1}]$ , shown in Fig. 5. Note that, as discussed in Ref. 16 these  $\phi$ -dependent structures do not satisfy the Lifshitz condition. So, either the transition is (slightly) discontinuous or the wave vector is not (exactly) equal to  $\mathbf{P}$ . The explanation for our omitting some of the structures found in Ref. 14 is the same as above.

We did not deal with the positions of the ions at the center of the octahedra or those between the layers of octahedra. Each such ion sits in a stable potential well. It is obvious that a displacement of these ions, consistent with the symmetry of the distorted structures we have found, must exist. The question is whether or not for systems without any accidental degeneracy there is a bifurcation so that additional space groups could be allowed when the positions of these “inessential” ions are taken into account. The stable potential well can be distorted and the placement of its minimum will be modified by the octahedral reorientation. But a single minimum of a stable potential well can not be continuously deformed into a double well without assuming an accidental vanishing of the fourth order term in the local potential. Similar

FIG. 5: (Color online) As Fig. 3 for the star of  $\mathbf{P}$  (variables change sign under  $z \rightarrow z + 1$ ).  $x, y$  are the tetragonal axes and  $X, Y$ , and  $Z$  are axes of the distorted structure. In each case the new origin is in the  $z = 1/4$  plane. The new out-of-plane lattice vector has magnitude 2.



arguments show that the perturbative effect of the other coordinates of the nearly rigid octahedra do not produce anomalous effects. It is true that in the spirit of the renormalization group the quartic potentials we invoke can be renormalized and thereby lead to modification, which if serious enough, could violate our arguments.

But the stiffer the octahedra are, the less likely such a scenario becomes. In any event, there is a regime for sufficiently large  $\lambda$  where our arguments are valid. The results of first principle calculations[20] indicate that the fourth order potential used here gives a nearly perfect description of the energy surface for octahedral rotations and, and at least for some systems, justify our analysis based on the Landau expansion up to quartic order. Many of the structures of Ref. 14 which we do not accept are those which arise from discontinuous transitions caused by higher than quartic terms in the free energy (which we omit). But several structures we omit (such as those with  $|\theta_1| \neq |\theta_2|$  or with disordered sublattices) are omitted because of the special form arising from the intraoctahedral constraint.

Experimentally, it is striking that the structures observed as distortions from the tetragonal phase are in our much shorter list. For instance, in the data cited on p 313 and ff of Ref. 17 five systems with  $\phi$  tilts are shown which go into either  $\text{Cmca}$  (64) or  $\text{P4}_2/\text{ncm}$  (138), except for  $\text{Rb}_2\text{CdCl}_4$  whose structure is uncertain: either  $\text{Cmca}$  or  $\text{Fccm}$  (which is on neither our list nor that of Ref. 14 because it involves two irreps). Systems (other than  $\text{Rb}_2\text{CdCl}_4$  subsequently discussed in Ref. 17) in Table III of Ref. 14 likewise go into either  $\text{Cmca}$  or  $\text{P4}_2/\text{ncm}$ .

To summarize: we find that the rigid octahedral constraint eliminates all the structures in Table I of Ref. 14 for which the octahedral tilting transitions are discontinuous and, in addition, those that are allowed by symmetry to be continuous but which involve disordered sublattices. Elsewhere we will give the results of our approach to encompass sequential phase transitions which involve two distinct irreps.

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- <sup>18</sup> Lengths are in units of lattice constants  $a_i$  and wave vectors in units of  $2\pi/a_i$ .
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